

## AN AQUEOUS SOLUTION OF A SODIUM SALT OF HEDTA

The invention relates to an aqueous solution of a sodium salt of the chelating compound HEDTA [N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid], to a container comprising said aqueous solution, and to the use thereof for making an iron-chelate complex. The invention further relates to a method  
5 for preparing such an aqueous solution of said sodium salt of HEDTA.

Some sodium salts of the chelating compound HEDTA are known in the art. For instance, in US 5,491,259 a method is disclosed for preparing HEDTA from the trisodium salt thereof (*i.e.* Na<sub>3</sub>-HEDTA). This method makes use of  
10 an acidic medium at pH 1.0 to 3.0, resulting in an aqueous feed solution containing fully protonated HEDTA along with an inorganic sodium salt. Subsequently, this aqueous solution is passed through a diafiltration membrane to separate the organic and inorganic components.

The disodium salt of HEDTA (*i.e.* Na<sub>2</sub>-HEDTA) is also known. For instance, in  
15 EP 0 054 277 and EP 0 058 430 microscopic capsules containing dyestuff suspensions with said disodium salt of HEDTA were disclosed.

K. Nakamoto *et al.* published the infrared spectra of HEDTA, and its mono-, di-, and trisodium salt in J. Am. Chem. Soc., 85, 311-312 (1963).

20 Commonly, when using HEDTA for chelating ions, the trisodium salt of HEDTA (Na<sub>3</sub>-HEDTA) is used. Thus, according to US 5,110,965 iron chelates can be made from a commercially available 41.3wt% aqueous solution of the trisodium salt of HEDTA by reacting an oxide of iron (as its magnetite) with Na<sub>3</sub>-HEDTA and acidifying the medium to a low pH value.

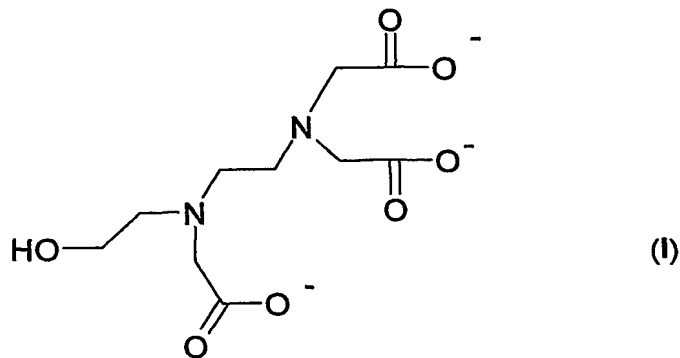
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However, the use of the trisodium salt of HEDTA has some major drawbacks when used on a commercial scale. An important problem is the high viscosity of concentrated solutions of the trisodium salt of HEDTA, which makes such

a solution difficult to handle. Thus, the high viscosity limits the practical concentration to values below 45wt%. Further, above certain concentrations, the trisodium salt of HEDTA tends to precipitate from the aqueous solution when being exposed to lower temperatures, making it necessary to heat the containers before the solution can be poured out. It was further found that aqueous  $\text{Na}_3\text{-HEDTA}$  solutions are corrosive to aluminum and therefore limits its application to corrosive-proof installations. These problems become particularly relevant when using HEDTA salt in large-scale productions, thus especially when containers with a content of 0.5kg or more are used. In practice containers can contain 25 to 1,000kg of aqueous HEDTA salt, or even more.

It is an objective of the present invention to provide an alternative for the aqueous solutions of the trisodium salt of HEDTA that has lower viscosity, does not precipitate at low temperature, can be handled in containers at higher concentrations, and has less corrosive properties.

The instant invention provides aqueous solutions of sodium salts of HEDTA satisfying the above conditions. To this end it was surprisingly found that the above-mentioned problems do not occur with an isolated aqueous solution of a sodium salt  $x\text{Na}^+ y\text{H}^+$  of the chelating compound of formula I:



wherein  $x = 2.1 - 2.7$ ,  $y = 0.9 - 0.3$ , and  $x + y = 3$ .

Furthermore, the present invention provides containers comprising at least 0.5kg of an aqueous solution of said sodium salt of HEDTA, since it was found that the above-mentioned problems do not occur in containers comprising at least 0.5kg of said solution. The term "container" as used  
5 throughout this specification is not only meant to include reservoirs in which the sodium salt of HEDTA according to the present invention can be stored and/or transported, but also tanks, barrels, drums, vessels, pipes or flush lines which can contain said sodium salt and which are used in a production  
10 process. The containers of the invention contain at least 0.5kg of the above solution, preferably at least 1kg, and most preferably 25kg or more. Preferably, said containers do not contain more than 2,000kg, more preferably 1,500kg of the above solution. Preferably, the containers comprising at least 0.5kg of the aqueous solution according to the present  
15 invention are made of PVC, polyethylene, stainless steel, or bituminized steel.

In order to use as less as possible acid for neutralization it is preferred to make an aqueous solution that is as close as possible to the trisodium salt,  
20 without having the disadvantages of the trisodium salt. It was found that an optimum regarding the use of neutralization acid, viscosity, precipitation and corrosive properties was obtained for  $x$  is about 2.4, for instance within the range 2.3 to 2.5.

It was furthermore found that the salt of the invention could be dissolved in  
25 water to a concentration of 45wt% or higher without impairing the hereinbefore-mentioned advantages. To satisfy the above conditions the aqueous solution has a pH between 7 and 11.

In another objective according to the invention there is provided in a use of  
30 the aqueous solution comprising the sodium salt  $x\text{Na}^+ y\text{H}^+$  of the chelating compound of formula I, wherein  $x = 2.1 - 2.7$ ,  $y = 0.9 - 0.3$ , and  $x + y = 3$ , for

preparing an iron-chelate complex. The preparation of this type of complex as such is known in the art, for instance as indicated above in US 5,110,965. When applying the aqueous HEDTA salt of the present invention, it is further clear to the skilled man how to make such complexes. Other metals than iron  
5 can also be complexed, such as other Group VIII metals, transition metals, rare earth metals, and the like. If Fe complexes are made, the aqueous HEDTA salt solution preferably contains 5-7wt% of the iron complex.

It is also an object of the invention to provide a method for making the above-mentioned aqueous HEDTA salt solutions. To this end the invention pertains to a method of preparing an aqueous solution comprising at least 45wt% of the sodium salt  $x\text{Na}^+ y\text{H}^+$  of the chelating compound of formula I wherein  $x = 2.1 - 2.7$ ,  $y = 0.9 - 0.3$ , and  $x + y = 3$  from the trisodium salt of N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid ( $\text{Na}_3\text{-HEDTA}$ ), comprising  
10 the step of electrodialysing at ambient temperature, *i.e.* 20°C, an aqueous solution containing less than 42wt% of  $\text{Na}_3\text{-HEDTA}$ , or at a different temperature at maximally the concentration whereby the viscosity is the same or lower than the viscosity of the 42wt%  $\text{Na}_3\text{-HEDTA}$  solution at 20°C using a bipolar membrane and a cation exchange membrane, thereby  
15 converting the  $\text{Na}_3\text{-HEDTA}$  solution into the solution of the sodium salt  $x\text{Na}^+ y\text{H}^+$  of formula I with  $x = 2.1 - 2.7$ ,  $y = 0.9 - 0.3$ , and  $x + y = 3$ .  
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Electrodialysis processes with bipolar membranes (EDBM) are known in the art. An overview of such processes can be found in M. Bailly, Desalination,  
25 144, 157-162 (2002). When using such process for making the sodium salt of HEDTA according to the present invention, preferably a caustic electrolyte is used, such as sodium or potassium hydroxide, sodium (hydrogen) carbonate, and the like. Suitable bipolar membranes are for instance Neosepta® BP1E from Tokuyama Corporation Ltd. (Japan), FT-BP™ from FumaTech GmbH  
30 (Germany) or Morgane® BPM from Solvay (Belgium). A cation exchange

membrane is used to separate the acid compartment from the base compartment and also to transport the sodium ions from the acid to the base compartment. Cation exchange membranes for this application should be acid and base stable. Suitable cation exchange membranes are for instance  
5 Neosepta® CMB (Tokuyama Corp.), FT-FKL™ and FT-FKB™ (both FumaTech GmbH) but any other cation exchange membranes can be used as long as these are acid and base stable and stable in the HEDTA solution under the conditions of the electrodialysis process.

10 The higher the temperature during electrodialysis, the lower the viscosity of the Na<sub>3</sub>-HEDTA solution. Thus, when higher temperatures are selected, higher concentrations than 42wt% of Na<sub>3</sub>-HEDTA can be used. However, when the viscosity of the solution becomes higher than the viscosity of a  
15 42wt% solution at 20°C, *i.e.* higher than about 25 cPoise, the transport of such a solution through the thin channels of electrodialysis cells is in general too much hampered to obtain an efficient process. It is therefore preferred to work at temperatures high enough to ensure that the viscosity is not higher than about 25 cPoise, but low enough to ensure that the membranes can still operate properly. When heat sensitive membrane types are used, the  
20 electrodialysis process is preferably performed at lower temperatures, down to room temperature.

The bipolar membrane electrodialysis process can be operated up to 90°C, which is the maximum temperature which most of the cation exchange  
25 membranes can stand. Preferably, the temperature should be below about 60°C when applying the FumaTech FT-BP™ or Morgane® BPM from Solvay bipolar membranes or below about 45°C when applying the Tokuyama Corp. Neosepta® BP1E bipolar membrane. From a practical point of view the process is most preferably performed at a temperature between 20 and  
30 45°C.

It is noted that due to electro-osmosis, water together with the sodium ions migrates from the HEDTA compartment through the cation exchange membrane into the caustic compartment. The HEDTA concentration therefore increases during the acidification process.

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It is furthermore noted that, although less preferred, the aqueous solution comprising at least 45wt% of the sodium salt  $x\text{Na}^+ y\text{H}^+$  of the chelating compound of formula I wherein  $x = 2.1 - 2.7$ ,  $y = 0.9 - 0.3$ , and  $x + y = 3$ , can also be prepared from  $\text{Na}_3\text{-HEDTA}$  by means of an electrolysis process comprising an electrochemical acidification step as for example described by P. Boyaval, J. Seta, and C. Gavach in Enzyme Microb. Technol., 1993, Vol. 15, August, p. 683-686.

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The invention is further illustrated with the following examples.

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#### Example 1

A  $\text{Na}_3\text{-HEDTA}$  solution with pH 11.05 and having a concentration of 41wt% of  $\text{Na}_3\text{-HEDTA}$  expressed as a Fe-TSV value (Iron Total Sequestering Value) was converted to the sodium salt  $x\text{Na}^+ y\text{H}^+$  of the chelating compound of formula I wherein  $x = 2.1 - 2.7$ ,  $y = 0.9 - 0.3$ , and  $x + y = 3$  by circulating the solution through a bipolar membrane (Neosepta® BP1; ex Tokuyama Corporation Ltd.) electrodialysis stack using a conventional pump. Due to the heat produced during the acidification process, the temperature of the HEDTA sodium salt solution increased from 30°C at the start of the experiment to 45°C at the end of the experiment. During the experiment, the pH-value in the HEDTA compartment was measured using a conventional calibrated pH-meter with a combined glass electrode. During acidification using said bipolar membrane electrodialysis stack, the pH-value of the HEDTA sodium salt solution decreased. It was found that when the pH had reached a value of 9.6 at a temperature of 35°C, the fluid flow of the HEDTA

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sodium salt solution, which was measured using a conventional flow meter, started to increase sharply from 40 l/h to over 200 l/h without changing the pump settings and/or other conditions. This indicates that the viscosity of the HEDTA sodium salt solution at the said conditions decreases sharply. The  
5 final HEDTA sodium salt solution that was obtained had a pH of 9.1, which corresponds with the sodium salt  $x\text{Na}^+ y\text{H}^+$  of HEDTA wherein  $x = 2.7$  and  $y = 0.3$ . The viscosity of said final solution measured with a Brookfield viscosity meter was 16.2 cPoise at 20°C and 7.7 cPoise at 50 °C.

#### 10 Example 2

Sodium salts  $x\text{Na}^+ y\text{H}^+$  of the chelating compound of formula I having various  $x$  and  $y$  values were prepared by acidification using the bipolar membrane  
15 electrodialysis stack as described in Example 1, until the desired pH value was obtained. The viscosity of the thus obtained HEDTA solutions was measured over a wide range of concentrations at two different temperatures (20°C and 50°C) using a Brookfield viscosity meter.

The Tables below show the viscosity (centiPoise) against HEDTA concentration (as Iron Total Sequestering Value, Fe-TSV, expressed as  $\text{Na}_3\text{-HEDTA}$  salt) for the  $x\text{Na}^+ y\text{H}^+$  salt of formula I in which  $x=3$  (comparative  
20 example),  $x=2.4$ , and  $x=2.1$ , and  $y=0$ ,  $y=0.6$ , and  $y=0.9$ , respectively.

**Table I.** Viscosity of HEDTA salts in relation to Fe-TSV at 20°C

<b>Concentration (wt%)</b>	<b>x=3 viscosity (cP)</b>	<b>x=2.4 viscosity (cP)</b>	<b>x=2.1 viscosity (cP)</b>
<b>10</b>	2	2	2
<b>30</b>	7.1	5.2	4.3
<b>40</b>	19	12.7	10
<b>50</b>	∞*	54	32.9

\* The viscosity of Na<sub>3</sub>-HEDTA at 50wt% could not be determined due to solidification of the product.

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At low concentration (10wt%) there was no significant difference measured in the viscosity between Na<sub>3</sub>-HEDTA (prior art) and Na<sub>2.4</sub>-HEDTA and Na<sub>2.1</sub>-HEDTA (this invention). At higher concentrations the viscosity differences became large. At 50wt% Na<sub>3</sub>-HEDTA could not be used anymore because it solidified, whereas both Na<sub>2.4</sub>-HEDTA and Na<sub>2.1</sub>-HEDTA could still easily be handled.

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**Table II.** Viscosity of HEDTA salts in relation to Fe-TSV at 50°C

<b>Concentration (wt%)</b>	<b>x=3 viscosity (cP)</b>	<b>x=2.4 viscosity (cP)</b>	<b>x=2.1 viscosity (cP)</b>
<b>10</b>	1	1	1
<b>30</b>	3.1	2.3	2.3
<b>40</b>	6.7	5.2	4.2
<b>50</b>	21.1	14.2	10.1



At higher temperature (50°C) the viscosity differences between Na<sub>3</sub>-HEDTA (prior art) and Na<sub>2,4</sub>-HEDTA and Na<sub>2,1</sub>-HEDTA, although smaller than at 20°C, remained.

5 The advantages of low viscosity are that it is easier to empty drums/containers, flush lines, maintain flows during pumping/handling the product, etc.

### Example 3

10 Transport classification of aqueous HEDTA solutions is also linked to corrosive potential. Corrosion tests carried out according to the NACE standard TM-01-69 using a 40wt% caustic-free Na<sub>3</sub>-HEDTA solution on aluminum 7075 T6 showed that the rate of corrosion to aluminum was above the allowed limit (max. average corrosion rate of 6.2 mm/year). This test with  
15 a 40wt% Na<sub>2,3</sub>H<sub>0,7</sub>- HEDTA aqueous solution gave an average corrosion rate for aluminum 7075 T6 of < 1 mm/year. This allows the product to be handled in aluminum containers and production equipment.